



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b>  <b>B41M 5/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/04981</b>  <b>(43) International Publication Date:</b> 4 February 1999 (04.02.99)
<b>(21) International Application Number:</b> PCT/US98/15153  <b>(22) International Filing Date:</b> 24 July 1998 (24.07.98)  <b>(30) Priority Data:</b> 08/899,562                      24 July 1997 (24.07.97)                      US  <b>(71) Applicant (for all designated States except US):</b> AVERY DENNISON CORPORATION [US/US]; 150 North Orange Grove Boulevard, Pasadena, CA 91103 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> SHIH, Frank, Yen-Jer [US/US]; 911 Palo Alto Drive, Arcadia, CA 91007 (US). LIN, Kenneth, S., C. [US/US]; 2890 Duarte Road, San Marino, CA 91108 (US).  <b>(74) Agent:</b> CARPENTER, John, D.; Christie, Parker & Hale, LLP, P.O. Box 7068, Pasadena, CA 91109-7068 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> INK-RECEPTIVE COMPOSITIONS AND COATED PRODUCTS		
<b>(57) Abstract</b>  Coatable ink-receptive compositions and coated substrates are provided. The compositions contain a pigment dispersed in a binder composed of an ethylene vinyl acetate emulsion polymer and at least one water soluble, cationic polymer, such as polydiallyldimethylammonium chloride and copolymers of a quaternary amino acrylate or methacrylate and hydroxy-lower alkyl acrylate or methacrylate. Papers, films, labels and similar products, coated with an ink-receptive composition, are also provided.		

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## INK-RECEPTIVE COMPOSITIONS AND COATED PRODUCTS

### 5 FIELD OF THE INVENTION

The present invention relates to coatable, water-based compositions for enhancing the ink-receptiveness of imprintable substrates, and coated products made with such compositions.

### 10 BACKGROUND OF THE INVENTION

As personal computers continue to grow in popularity and use, demand for high quality peripherals, such as printers, and associated components, such as paper and label stock, also continues to grow. A variety of printers are known, including dot matrix, laser, and ink jet printers. In recent years, ink jet printers have enjoyed growing popularity, in part due to the  
15 availability of colored inks.

As computer technology has improved and developed, and new software and printer designs have enabled a tremendous variety of fonts, designs, and even photographs to be printed with computer printers, demand for high quality films, papers, labels, and similar imprintable substrates has also grown. Although efforts have been made to produce high  
20 quality ink-receptive sheet materials, such as films, papers and labels, a continuing need exists for high quality, ink-receptive constructions, particularly ink jet-imprintable constructions, characterized by high resolution, high color density, good color gradation, and other print qualities, as well as a need for materials that facilitate fast drying of water-based inks, smudgeproofness, waterfastness, and compatibility with both pigment-based and dye-  
25 based inks. The ideal product should be low cost and easily processed, and usable with a variety of inks and printing conditions.

### SUMMARY OF THE INVENTION

In accordance with the present invention, coatable, ink-receptive compositions and  
30 coated products are provided. In one embodiment, an ink-receptive, coatable composition comprises a pigment dispersed in or mixed with a binder which comprises an ethylene-vinyl acetate emulsion polymer and at least one water soluble, cationic polymer. The cationic polymer fixes acid dye colorants in water-based inks, and diminishes dye diffusion. Preferably, the binder includes at least two water soluble, cationic polymers, namely, (1) a  
35 polymerized diallyldimethylammonium compound and (2) a copolymer of dimethylaminoethyl acrylate or methacrylate and at least one hydroxy-lower organic acrylate or methacrylate, with hydroxyethyl acrylate (HEA) and hydroxyethyl methacrylate (HEMA) being most preferred. In some embodiments, a nonionic or cationic surfactant is included

within the binder mixture to enhance print quality of the coating. A preferred ink-receptive composition has, on a percent by weight (dry weight) basis, about 15-70% EVA emulsion polymer, about 5-50% of at least one water soluble, cationic polymer, about 20-60% pigment(s), and up to about 10% of one or more surfactants.

When coated on paper or film face stock or label stock, the ink-receptive compositions provide coated products that work particularly well with ink jet printers and have a high degree of ink-receptivity toward both pigment-based and dye-based inks, colored as well as black. Improvements are seen in color density, resolution, color gradation, drying time, smudgeproofness and water-fastness. Printed images on the coated products provided by the invention are crisp and have very low bleed. The coatings tend to be hydrophilic, yet water resistant, and quickly absorb water-based inks without becoming tacky or suffering a loss of integrity.

In one aspect of the invention, a water resistant, wide format or narrow format graphic construction suitable for use indoors or outdoors is provided, and comprises a substrate having first and second surfaces (or multiple inner and outer surfaces), an ink-receptive coating as described herein on the first surface of the substrate, an inked image imprinted on the coated substrate, and an adhesive coated on or applied to the second surface of the imprinted substrate. Ink jet-imprinted graphic constructions are readily made using wide format or narrow format ink jet printers. Once made, the constructions can be adhered to any object having a surface capable of receiving the constructions, such as billboards, other outdoor signage, the walls of buildings, buses, etc.

## DETAILED DESCRIPTION

The present invention provides coatable, ink-receptive compositions and coated products, such as papers, films, labels and similar constructions. In one embodiment, an ink-receptive composition comprises a pigment dispersed in a binder which comprises an ethylene-vinyl acetate ("EVA") emulsion polymer and at least one water soluble, cationic polymer.

EVA polymers (more precisely, copolymers) are generally hydrophobic (in bulk), have glass transition temperatures ( $T_g$ ) ranging from about  $-15^{\circ}\text{C}$  to  $25^{\circ}\text{C}$ , and tend to form films at relatively low temperatures. In contrast, vinyl acetate homopolymer has a  $T_g$  of about  $30^{\circ}\text{C}$ , and does not form films at room temperature.

Where the composition is to be applied to a paper substrate, it is preferred that the composition have a high solids content, in order to minimize curling of the paper substrate during the coating process, and to ease drying of the coating. High solids content EVA emulsion polymers are available from Air Products & Chemicals, Inc., Allentown, PA, under

the AIRFLEX trademark. Examples include AIRFLEX 465™ (65% solids) and AIRFLEX 7200™ (72-74% solids). Another suitable EVA emulsion polymer is AIRFLEX 426™, a high solids, carboxylated, EVA polymer partially functionalized with carboxyl groups. This polymer is thought to improve the water resistance of the resulting ink-receptive coating, particularly when the coated substrate is imaged with a dye-based ink. It is believed that the AIRFLEX brand EVA emulsion polymers are stabilized with up to about 5% by weight polyvinyl alcohol (PVOH) and/or, in some formulations, a nonionic surfactant. EVA emulsion polymers used in the present invention preferably have a solids content of from about 40 to 75%.

The EVA emulsion polymer preferably comprises from about 15 to 70%, more preferably from about 25 to 65% by weight of the ink-receptive composition, on a dry weight basis (meaning that water is not included in the calculation of the compositional percentages).

Water soluble, cationic polymers useful in the practice of the present invention include, but are not limited to, quaternary ammonium polymers (also known as polyquaternary ammonium salts, polyquats and quaternary polymers). Nonlimiting examples of quaternary ammonium polymers include polydiallyldimethylammonium compounds and copolymers of quaternary dimethylaminoethyl acrylate or methacrylate and one or more hydroxy-lower organic acrylate or methacrylate, for example, hydroxyethyl acrylate (HEA) and hydroxyethyl methacrylate (HEMA). To maintain charge neutrality, a monovalent or divalent counterion, Z, is associated with each quaternary ammonium center. Nonlimiting examples of such counterions include halides, (for example, chloride) and dimethylsulfate anion.

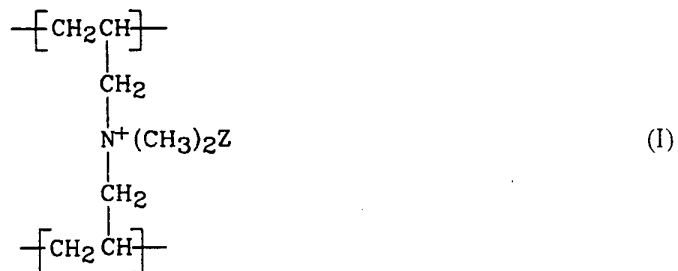
As used herein, the term "hydroxy-lower organic acrylate or methacrylate" refers to an acrylic or methacrylic acid ester, the ester group of which is a straight - or branched-chain alkyl, alkenyl, alkynyl or ether group containing from 1 to about 6 carbon atoms, substituted with at least one hydroxy group at a primary or secondary carbon. Nonlimiting examples of such groups include hydroxy-substituted methyl, ethyl, propyl, vinyl, allyl and propynyl groups.

A particularly preferred, water soluble, cationic polymer is poly(diallyldimethylammonium chloride) (PDADMAC), available from CPS Chemical Co., (Old Bridge, NJ) as a low, medium, or high molecular weight polymer. In general, low molecular weight, water soluble, cationic polymers are preferred, as they tend to have lower viscosities and allow high solids content formulations to be prepared without sacrificing coatability. The chloride ions in PDADMAC can be exchanged for different monovalent or divalent counterions by, e.g., dissolving the polymer in a suitable solvent and passing the solution through an ion exchange resin. Poly(diallyldimethylammonium dimethyl sulfate) is

another preferred, water soluble, cationic polymer.

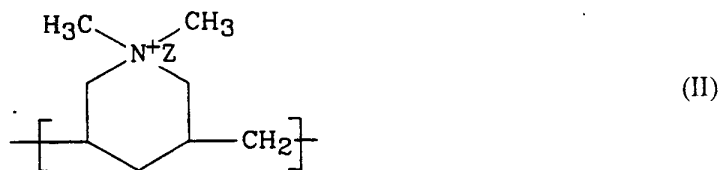
Although not bound by theory, it is believed that poly(diallyldimethylammonium) compounds have a variety of polymer geometries which depend on the manner in which individual monomers link up during polymer chain propagation. Representative, nonlimiting examples of the repeat units for such polymeric compounds include formulas (I)-(III) and mixtures thereof:

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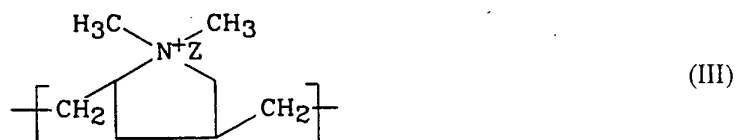
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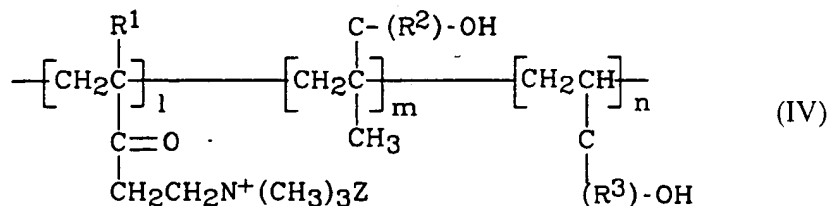
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where Z is as defined above.

Other preferred, water soluble, cationic polymers include copolymers of quaternary dimethylaminoethyl acrylate or methacrylate and one or more hydroxy-lower organic acrylate or methacrylate, which have the general formula (IV) :



wherein R<sup>1</sup> is hydrogen or methyl; (R<sup>2</sup>-OH) and (R<sup>3</sup>-OH) are, independently, lower alkyl, alkenyl, alkynyl or ether substituted with a hydroxyl group at a 1° or 2° carbon; l > 0; m ≥ 0; n ≥ 0, provided that m and n are not both zero; and Z is as defined above.

Water soluble, cationic polymers of formula (IV) can have a variety of geometries, depending on whether the individual monomers are polymerized head-to-head, head-to-tail, randomly, in fixed sequence (e.g., ABABAB...), in blocks, or in some other manner. No specific geometric arrangement of monomers is intended by the formulas presented herein.

Copolymers of quaternary dimethylaminoethyl acrylate or methacrylate and one or more hydroxy-lower alkyl acrylate or methacrylate are prepared using standard polymerization techniques, for example, free radical polymerization. Thus, a terpolymer of quaternary dimethylaminoethyl acrylate (DMAEA), hydroxyethyl acrylate and hydroxyethyl methacrylate is readily made by heating a mixture of the monomers in the presence of a free radical initiator, optionally by varying the rate of addition of monomers and/or initiator to the reaction mixture. As but one nonlimiting example, a preferred terpolymer of HEA, HEMA and quaternary DMAEA (with DMS as counterion), may comprise, on average, from about 18 to 37 HEA monomer units, 52 to 74 HEMA monomer units, and about 5 to 17 quaternary DMAEA monomer units.

Nonlimiting examples of suitable polymerization initiators include water- and/or alcohol-soluble initiators, for example persulfates, such as sodium persulfate and potassium persulfate; peroxides, such as hydrogen peroxide and tert-butyl hydrogen peroxide; and azo

compounds, such as VAZO™ initiators; used alone or in combination with one or more reducing agents or activators.

5 To control polymer chain length, a chain transfer agent or other molecular weight regulator can be added to the polymerization mixture. Nonlimiting examples include 2-mercapto ethanol, n-dodecyl mercaptan (n-DDM), t-dodecyl mercaptan (t-DDM), monothioglycerol, mercapto acetates, and long chain alcohols. Water soluble chain transfer agents, such as 2-mercapto ethanol, are preferred. In some embodiments, a small amount of  
10 polyethylene glycol (e.g., PEG 1000) or similar nonionic, water soluble polymer can be added to the reaction mixture as a dispersion medium and/or to increase the solids content of the resulting polymer.

The water soluble, cationic polymer(s) comprise(s) from about 5 to 50% by weight (on a dry weight basis) of the coatable formulation, with a mixture of cationic polymers being  
15 preferred. More preferably, the water soluble, cationic polymer comprises a mixture of about one-third poly(diallyldimethylammonium) compound and two-thirds copolymer of quaternary dimethylaminoethyl acrylate or methacrylate and one or more hydroxy-lower organic acrylate or methacrylate.

In a preferred embodiment of the invention, the binder further includes one or more  
20 cationic or nonionic surfactants, which help to wet the pigment and/or enhance print quality of the resulting composition. Nonlimiting examples of nonionic surfactants include alkylphenol ethoxylates, such as nonylphenol ethoxylate, and Disponil A 3065, an ethoxylated nonionic surfactant available from Henkel of America Inc. (King of Prussia, PA). A nonlimiting example of a cationic surfactant useful in the practice of the invention is  
25 hexadecyl trimethylammonium chloride (HDTMAC), available from Akzo Nobel Chemicals Inc. (Chicago, IL). Anionic surfactants should be avoided because of their likely electrostatic interaction with the cationic, water soluble polymer(s).

Preferably, up to about 10% by weight (on a dry weight basis) of one or more  
30 surfactants is employed in the ink-receptive composition. Too much surfactant can potentially cause the coating to have air bubbles, which could adversely effect print quality when coated on film substrates. Other components, such as thickeners and defoamers can be added to the formulation to improve processability.

Pigments useful in the ink-receptive compositions of the present invention include materials that increase the opacity and/or modify the porosity of the coated substrate.  
35 Inorganic pigments are especially preferred; nonlimiting examples include silica (preferably, amorphous silica gels), silicic acid, clays, zeolites, alumina, TiO<sub>2</sub>, M<sub>6</sub>CO<sub>3</sub> and the like. The pigment increases the ink-absorbitivity and improves the print quality and water resistance of the dried coating, and enables the coating to be used with water-based inks containing a dye



colorant, as well as pigmented, water-based inks. Preferred ink-receptive compositions prepared in accordance with the present invention contain from about 20 to about 60% by weight pigment, based on the dry weight of EVA emulsion polymer, water soluble, cationic polymer, and pigment. Below about 20% by weight pigment, print quality may suffer, though this can be controlled, in part, by adjusting average particle size of the pigment and/or the binder-to-pigment ratio. Without pigment in the composition, drying rates of some inks printed on the coated substrate tend to be undesirably low. However, in those applications where drying time is less of a concern, the pigment can be omitted.

In addition to the pigment(s) included to increase the opacity and/or modify the porosity of the coated substrate, in one embodiment of the invention an additional pigment is added to increase the adhesion of the coating to the substrate and, preferably, to balance the overall properties of the coating, including, for example, improvement of the cohesive strength of the coating. A preferred but nonlimiting example of such a pigment is a colloidal dispersion silica, such as Ludox CL-P™, available from DuPont de Nemours, E.I., Co. (Wilmington, DE).

Coatable, ink-receptive compositions are readily prepared by blending surfactant, EVA emulsion polymer, quaternary ammonium polymer(s), and pigment(s), preferably in that order. More preferably, additional surfactant is added prior to the introduction of pigment to the formulation.

In a second aspect of the invention, ink-receptive coated constructions or products, such as papers, cardboard, corrugated boards, films, labels, and other porous or nonporous substrates are provided, and comprise substrates coated with an ink-receptive composition as described herein. When cut to size, the coated products are particularly well suited for use in ink jet and other printers and provide excellent print quality when imprinted with black, as well as colored, water-based inks, including inks colored with either a pigment or a dye.

Both "wide format" and "narrow format" ink-receptive products are encompassed by this aspect of the invention. Wide format products are generally manufactured as wide rolls (24 or more inches wide), and are roll-fed into large printers for imaging. They are typically employed in commercial settings, and include, without limitation, movie theater posters, outdoor signage, large advertisements, and the like. Narrow format products are generally manufactured as narrow rolls or individual sheets, and can be roll-fed or sheet-fed into printers for imaging. They are typically used in the office or home, and include, without limitation, computer printer paper, labels, transparencies, and the like.

Wide format and narrow format ink-receptive products differ not only in size, but also in ink capacity, durability, and other properties, and are often exposed to different use environments. For example, wide format products may encounter more ink per unit area

when run through certain commercial printers. Problems with poor image quality, color bleed, and smearing can be avoided by enhancing the ink-absorbitivity of the impritable substrate--for example, by adding more pigment to the coating composition.

Durability, including waterfastness, resistance to light-induced fading, abrasion resistance, color stability, and other properties also can differ between wide format and narrow format products. The present invention is intended to meet the more rigorous demands placed on wide format products, including products intended for outdoor use, as well as the durability demands placed on narrow format products. To improve overall durability of the composition, the binder can be modified by adding a crosslinker. Suitable crosslinkers include, without limitation, multifunctional polyisocyanates, melamine formaldehyde resins, and urea formaldehyde resins. Although not bound by theory, it is believed that such crosslinkers promote the formation of network structures during or after drying of the compositions on the face stock or label stock.

Coatable substrates useful in the practice of the present invention include paper, cardboard, corrugated board, plastic film, and metal film or foil face stocks and label stocks traditionally used for ink printing applications, particularly ink jet printing. Self-wound materials and other linerless products are also suitable substrates. Nonlimiting examples include self-wound tapes. Nonlimiting examples of paper face stocks suitable for use with the present invention include offset, bond, text, cover, index, lightweight printing paper, litho paper, and sulfite paper. Although not required, a surface treatment, such as starch, sizing agents, and the like, can be included on the paper substrates. Nonlimiting examples of plastic face stocks suitable for use with the present invention include polystyrene, polyvinyl chloride, polyester, nylon and polyolefin (for example, polyethylene) films. Polymer blends are also included in this list of examples. The films may be cast, extruded, or coextruded. A film substrate comprising a coextruded polyolefin-polybutylene terephthalate sandwich can be used in the present invention. A nonlimiting example of a metal face stock suitable for use with the present invention is aluminum foil.

Coatable label stocks useful in the practice of the present invention include without limitation, a variety of printable label constructions or assemblies well known in the art, each typically comprising a label face stock (sheet or roll) having at least one inner and at least one outer surface, a pressure-sensitive adhesive (PSA) adhered to at least one inner surface of the label face stock, and a removable release liner abutting the PSA, the entire assembly forming a sandwich-like construction.

An ink-receptive coated product is easily made by applying an ink-receptive composition as described above to one or both surfaces of a face stock or label stock, using a conventional coating or other application technique. Nonlimiting examples of such

techniques include slot die, air knife, brush, curtain, extrusion, blade, floating knife, gravure, kiss roll, knife-over-blanket, knife-over-roll, offset gravure, reverse roll, reverse-smoothing roll, rod, and squeeze roll coating. The composition can also be applied to paper substrates in a size press, during paper manufacture. For label products, the composition can be applied using any conventional technique or process, including without limitation, coating "on-press" during the converting process (e.g., in concert with the processes of die-cutting, matrix stripping, etc.), coating off-press using a separate coater, and other application methods.

In general, dry coat weights of from about 5 to 70 g/m<sup>2</sup> are preferred, depending on the particular face or label stock employed. Thus, coated paper face stocks are advantageously prepared with composition coat weights of from about 5 to 30 g/m<sup>2</sup>, more preferably about 15 to 25 g/m<sup>2</sup>. Vinyl (PVC) substrates are more preferably coated with from about 40 to 70 g/m<sup>2</sup> of ink receptive composition.

Using the ink-receptive compositions and coated products described herein, high quality imprinted constructions are prepared by running the constructions through a printer and imprinting an image thereon. Advantageously, the compositions and coated products are designed to perform well with a variety of printer technologies including, without limitation, piezoelectric printer heads, thermal imaging, drop on demand, and other technologies. A particularly preferred aspect of the invention is the finished product -- an imprinted (inked) construction comprising a face or label stock having at least one inner surface and at least one outer surface, imprinted with a high quality black and/or colored image. As but one example, this aspect of the invention is embodied by an ink jet-imprinted construction comprising a porous or nonporous substrate (face stock or label stock), coated with an ink-receptive composition and imprinted with an ink image. In some embodiments, the construction is die cut.

### EXAMPLES

The following nonlimiting examples are illustrative of the invention.

#### Polyquat A

A monomer mixture consisting of 40g HEA, 100g HEMA and 40g of an 80% by weight aqueous solution of quaternary dimethylaminoethyl acrylate - dimethyl sulfate ("DMAEMA-DMS, 80% active") was prepared, with stirring, and contained, on a percent by weight (dry weight) basis, 23% HEA, 58% HEMA and 19% DMAEMA-DMS.

A 4-neck, 1000ml flask equipped with a thermometer, stirrer and condenser was charged with 100g H<sub>2</sub>O, 60g polyethylene glycol 1000 and 16% of the monomer mixture (29g), and heated to 60°C, at which time 5g of a mixture of 27g H<sub>2</sub>O and 3g sodium persulfate was added.

The contents of the flask were heated to 95°C and, 5 min. later, the remainder of the monomer mixture was added over a 100 min. period. Simultaneously, 25g of the persulfate/water mixture was added over a 120 min. period.

The contents of the flask were held at a constant temperature of 95°C for one additional hour, and then 70g H<sub>2</sub>O was added, thereby cooling the mixture.

When the temperature rose to 60°C, 0.5g of a 30% by wt. aqueous solution of H<sub>2</sub>O<sub>2</sub> was added, and a mixture of 15g H<sub>2</sub>O and 0.5g sodium formaldehyde sulfoxylate (a redox agent) was slowly added over 15 min. Another 0.5g H<sub>2</sub>O<sub>2</sub> was then added, the contents of the flask were allowed to cool, and aqueous NaOH (10% by wt.) was added to raise the pH of the polymeric solution to 5.

### **Polyquat B**

A copolymer of 17% HEA, 45% HEMA and 64% DMAEMA-DMS was prepared in the same manner as Polyquat A, except the monomer mixture consisted of 30g HEA, 78g HEMA and 80g of an 80% active solution of DMAEMA-DMS.

### **Coatable, Ink-Receptive Compositions**

#### **Examples 1 and 2 and Comparative Example 1**

In Example 1, a coatable, ink-receptive composition containing a single cationic, water soluble polymer (PDADMAC) was prepared by blending the following components together in the order listed: 2g Disponil A 3065, 18g Airflex 7200 EVA emulsion polymer, 5g Agefloc Wt50SLV (a poly(diallyldimethylammonium chloride from CPS Chemical Co.)); 2g hexadecyl trimethylammonium chloride (HDTMAC); and 10g Silcron G-100 (a silica powder available from SCM Chemical). The resulting composition had a solids content of 38.2% (by weight).

In Example 2, a coatable, ink-receptive composition was prepared as in Example 1, except 10g of Agefloc Wt50SLV was used. Solids content was 40.6%.

As a control, Comparative Example 1 (C-1), a coatable, ink-receptive composition, was prepared as in Example 1, except that no PDADMAC was included and 25g Airflex 7200 was used. Solids content was 35.0%.

#### **Examples 3 and 4**

In Example 3, a coatable, ink-receptive composition containing two cationic, water soluble polymers (PDADMAC and Polyquat A) was prepared by blending the following components together in the order listed: 2g Disponil A 3065; 9g Airflex 7200; 10g Agefloc

Wt50SLV; 20g Polyquat A; 2g HDTMAC; and 8g Silcron G-100. Solids content was 38.8%.

5 In Example 4, a coatable, ink-receptive composition was prepared as in Example 3, except 18g Airflex 7200, 5g Agefloc Wt50SLV, 10g Polyquat A, and 10g Silcron G-100 were used. Solids content was 42.2%.

#### **Example 5**

10 In Example 5, a coatable, ink-receptive composition containing a single water soluble, cationic polymer (Polyquat B) was prepared by blending the following components together in the order listed: 2g Disponil A 3065; 18g Airflex 7200; 15g Polyquat B; 2g HDTMAC; and 10g Silcron G-100. Solids content was 42.2%.

#### **Examples 6 and 7**

15 In Example 6, a coatable, ink-receptive composition containing two water soluble, cationic polymers (PDADMAC and Polyquat B) was prepared by blending the following components together in the order listed: 2g Disponil A 3065, 18g Airflex 7200; 5g Agefloc Wt50SLV; 10g Polyquat B; 2g HDTMAC; and 10g Silcron G-100. Solids content was 42.2%.

20 In Example 7, a coatable, ink-receptive composition was prepared as in Example 6, except 10g Agefloc Wt50SLV was used. Solids content was 41.7%.

#### **Example 8**

25 In Example 8, a coatable, ink-receptive composition was prepared as in Example 4, except Gasil® HP39 (a synthetic, amorphous silica gel, available from Crosfield Company (Joliet, IL)) was used as pigment, with minor differences in the quantities of the other ingredients.

30 Table 1 provides a summary of the formulations of Examples 1 to 8 and Comparative Example 1, with the relative amount of each component expressed as a percentage by weight, on a dry weight basis.

35

**TABLE 1**  
**Formulation by Percentage of Dry Weight**

Example	Disponil A 3065	Airflex 7200	Agefloc Wt50SLV	Polyquat A	Polyquat B	HDTMAC	Silcron G-100	Gasil HP39
C-1	4	61	-	-	-	2	33	-
1	5	48	9	-	-	2	36	-
2	4	44	17	-	-	2	33	-
3	4	21	16	32	-	2	25	-
4	4	40	8	15	-	2	31	-
5	4	40	-	-	23	2	31	-
6	4	40	8	-	15	2	31	-
7	4	38	14	-	14	2	28	-
8	3	36	7	14	-	2	-	38

#### Coatable Products

To evaluate the ink-receptivity of the compositions described above, a series of coating and printing trials were conducted, using paper labels coated with the compositions of Examples 1 to 7 and C-1. The labels had the following characteristics:

#### Label Stock

- Type: uncoated litho paper, pre-primed with 30% polyvinyl acetate and 70% silicate (primer coated on one side to enhance adhesion of the PSA)
- Basis weight: 50 lb/ream
- Caliper:  $4.3 \pm 0.25$  mil (approx. 0.1mm)
- Sizing: none
- Dimensions: 25 x 38 in. (63.5 x 96.5 cm)
- Manufacturer: CBC Coating, Inc., Neenah, WI

#### PSA

- Type: removable acrylic-based PSA
- Coat weight:  $11 \pm 1$  g/m<sup>2</sup>
- Manufacturer: Avery Dennison Corporation

#### Release Liner

- Type: Presiliconized release liner, one side silicone coated

- Basis weight: 50 lb/ream
- Caliper:  $3.2 \pm 0.3$  mil (approx. 0.08 mm)
- 5 •Manufacturer: Rhineland Paper, Rhineland, WI.
- Dimensions: 25 x 36 in. (64 x 91 cm)

Each of eight label constructions was coated on its imprintable surface (the face opposite the release liner) with one of the compositions of Examples 1 to 7 and C-1, using a slot die coater. Coat weights were about  $25 \text{ g/m}^2$ , measured after drying in an oven heated to 180°F (82°C).

Each coated construction was fed through a Hewlett Packard 820CSE Color Desk Jet, 4-color, ink jet printer having water-based inks with dye colorants (except black, which was pigmented); printed with an image; and evaluated for color density (a dimensionless measurement of the light reflection density of the printed image), in an IQ-150 Graphics Arts densitometer, manufactured by Tobias Associates, Inc. Within a particular region characterized by a specific color, three or four independent measurements of color density were taken. The measurements were averaged, and the results are presented in Table 2. High color densities are preferable to low color densities, and a difference of 0.05 units or more is considered significant.

**TABLE 2**  
**Color Density on Paper Labels**

Example	Blue	Green	Magenta	Black	Yellow	Red	Cyan
C-1	1.39	1.27	1.36	1.45	1.05	1.15	1.43
1	1.57	1.43	1.50	1.46	1.10	1.25	1.62
2	1.58	1.45	1.52	1.47	1.16	1.25	1.65
3	1.60	1.57	1.57	1.29	1.25	1.42	1.58
4	1.53	1.44	1.45	1.46	1.13	1.28	1.52
5	1.50	1.30	1.44	1.44	1.11	1.20	1.60
6	1.57	1.51	1.52	1.48	1.17	1.30	1.58
7	1.62	1.51	1.57	1.48	1.22	1.33	1.62

As shown in Table 2, each of the examples exhibited color densities higher than those exhibited by the control. Compositions formulated with Polyquat A or B performed particularly well.

### Comparative Testing on a Variety of Printers

- 5       Samples of three different ink jet products were fed through 16 different ink jet printers, printed with an image, and evaluated for overall print quality, ink drying time, optical density and waterfastness.

#### Printers

- 10       The following ink jet printers were used to test different ink jet printable products: Hewlett Packard - HP500C, 560, 682C, 693C, 850C, 1200C, and 1600C; Canon (Bubble Jet) BJ-200e, BJC-600, BJC 4200, BJC 4200 photo, and BJC 4200 Neon; Epson Stylus Color II, 500 and 1500. The "Plain Paper" and "Normal" print quality settings were selected on the printer drivers.

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#### Test Methods and Equipment

- Evaluations of black and color print quality (PQ) were made using a GTI Color Matcher, Model CMB, color matching booth, with a D65 setting, in the following areas:  
20       black text and solid (area) fills; color text and solid (area) fills; color to color bleed; and color intensity of green, yellow, cyan, magenta and red color fills. Ambient temperature and relative humidity were 72 °F (22 °C) and 50%, respectively.

- Optical density and waterfastness were measured using an X-rite densitometer, Model No. 428. For those printers with pigmented black inks, the drip test for image permanence  
25       was performed on black, cyan, magenta and yellow. For all other printers, the drip test was performed on black ink only.

- The overall print quality (PQ) of printed text, denoted A1 (black) and C1 (color), represents a combination of two properties of printed text: feathering/wicking and spraying. Feathering/wicking is a common characteristic of ink-paper interactions that cause  
30       degradation in print quality. The primary phenomenon is one of ink flow along the length of paper fibers, causing protrusions out of the main body of the text. It causes fuzzy edges, spidery lines and poor print quality. Spraying is a characteristic of the printer type and the paper, and occurs when ink splatters or sprays outside of the test region. It shows up in the trailing edge of the print. To evaluate these two properties, a short word or phrase was  
35       printed and the text was examined under 5X magnification. Overall print quality was expressed by rating the level of feathering/wicking and spraying using a 4-point scale, wherein 1=severe; 2=moderate; 3=slight; and 4=no feathering/wicking or spraying.

      The overall print quality (PQ) of printed solid regions or graphics, referred to as "area



fill" and denoted B1 (black) and D1 (color) represents a combination of three properties of printed graphics: mottling, cascading and bronzing. Mottling refers to a non-uniformity in printing that occurs when ink follows patterns in the paper as a result of non-uniform ink-paper interactions. This leads to non-uniformity of the image density. Cascading is a deficiency in coverage of a 100% area fills. It manifests itself as low density bands between print swaths. Bronzing is a characteristic of ink-paper interactions that manifests itself as a bronze sheen in area fills. To evaluate printed solid regions or graphics for these characteristics, the solid area of a black or colored region of a printed sample was compared to a control sample: a color optimized ink jet label sheet having no die-cuts (equivalent to label product nos. 8250 and 8253, sold by Avery Dennison Corporation). Overall area fill print quality was then evaluated by rating the level of mottling, cascading and bronzing using a 4-point scale, wherein 1=severe, 2=moderate, 3=slight, and 4=no mottling, cascading and/or bronzing.

Printed color graphics were also evaluated for color-to-color bleed, denoted D2, a common characteristic of ink-paper interactions that cause a degradation in print quality wherein one color bleeds into an adjacent color. Black-to-yellow color bleed is the most noticeable. This characteristic was measured by evaluating (a) line growth, an increase in the width of a printed line, and (b) edge roughness, protrusions out of the main body of a line into the adjacent background color. To evaluate color-to-color bleed, a multicolor graphic image was printed, preferably as a yellow, red and green object outlined in black. Using a magnification of 5X, the sample was evaluated for bleed areas and compared to the performance of the Avery Dennison color optimized control sample identified above. The results were expressed using a 4-point scale, wherein 1=severe (unacceptable), 2=moderate, 3=slight, and 4=no color-to-color bleed.

Overall color intensity of the colors blue, green, yellow, cyan, magenta, and red was evaluated by printing a color image and examining it for overall appearance of each color. A 4-point scale was used to rate the color intensity, wherein 1=dull, 2=average, 3=bright, and 4=very bright.

Total numerical values for the print quality evaluations are also presented, and represent a weighted average of the ratings, namely, A1, B1 and C1 each contribute 25% of the overall total numerical value, and D1, D2 and D3 each contribute 8.3% of the total numerical value.

Ink drying times (in minutes and seconds) were measured for black text (A2), black graphics, or , area fill (B3), color text (C2), and color graphics or area fill (D4). In each test, a textual or graphic image was printed on a sample media. As the sample was ejected from the printer, a timer was started and the sample placed print side up on a flat surface. At the same

time, the printed page was gently wiped with a Kimwipe™, without added force, across the printed text or solid area fill. If no ink was transferred to the Kimwipe™, the drying time was recorded as zero. If the Kimwipe™ showed any ink transfer, the imaged region was checked at 5 second intervals, with wiping, until no more ink transferred to the Kimwipe™. The total elapsed time required to dry the ink was recorded.

The image permance of black images was evaluated by measuring optical density, denoted B3, in the manner described above, and by measuring waterfastness, denoted E1, using a drip test. Waterfastness is an expression of the amount of (black) colorant transferred from a printed area to an unprinted area when deionized water is dispensed at a 45° angle on a printed sample. A sample was printed with a series of parallel bars and allowed to dry for 1 to 1.25 hours, then placed at a 45° angle such that the bars were horizontal. A 250μL pipette was filled with deionized water, and its tip was placed 5-10 mm above the top horizontal bar of the printed sample. The water in the pipette was then dispensed on to the sample. A second drip was commenced in the same way, starting about 2.5 mm from the first drip line (a vertical path down the sample) without allowing the streams to merge. 15 seconds after the second drip was dispensed, the sample was removed to a flat surface and allowed to dry for at least 10 minutes. Thereafter, the optical density of the transferred colorant was measured with a densitometer, taking 5 readings at just below each of the first 5 horizontal bars, for each of the two drips. (A 4mm aperture reflective densitometer was used.) The optical density measurements were averaged, for each of the two groups. Similarly, optical density readings from an un-imaged area of the sample were taken (drip 2). Water resistance was calculated by subtracting the measurements obtained above (drip 1 minus drip 2), and comparing the results with the color-optimized Avery Dennison control sample identified above.

The waterfastness, E1, of yellow, cyan and magenta colored images was also evaluated, using the drip test procedure described above.

### 30 **Example 9**

In Example 9, several samples of a glassine ink-jet paper label product (Avery Dennison 8800) were coated in a slot die coater with an ink-receptive composition containing PDADMAC and Polyquat A (prepared as in Example 4), to a dry coat weight of about 25 g/m<sup>2</sup>; printed with an image in several ink jet printers; and evaluated for print quality, color intensity, drying time and image permanence (waterfastness). The results are presented below in Tables 3 and 4.

**Comparative Example 2**

5 In Comparative Example 2 (C-2), several samples of an uncoated, glassine ink jet paper label product (Avery Dennison 8800) were printed with an image in several ink jet printers, and evaluated for print quality, color intensity, drying time and image permanence. The results are presented below in Tables 5 and 6.

**Comparative Example 3**

10 In Comparative Example 3 (C-3) several samples of a 1.5 mil thick, coated, matte finish polyester sheet, available from PCI were printed with an image in several ink jet printers, and evaluated for print quality, color intensity, drying time and image permanence. The results are presented below in Tables 7 and 8.

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**Table 3**  
**Print Quality (PQ) and Color Intensity -- Example 9**

PRINTER	BLACK		COLOR				Total Numerical	COLOR INTENSITY						
	TEXT	AREA FILL	TEXT	AREA FILL				AREA FILL D3						
				B1 Overall PQ	D1 Overall PQ	D2 C to C Bleed		D3 Color Intensity	Blue	Green	Yellow	Cyan	Magenta	Red
HP 500C	3	3	3	3	4	3	3.13	2	2	3	3	3	2	
HP 560C	2	3	3	4	4	3	2.88	3	2	3	3	3	2	
HP 682C	2	4	3	3	4	3	3.13	3	3	2	3	3	3	
HP 693C	3	3	3	3	4	4	3.25	4	4	4	4	4	4	
HP 850C	2	3	3	2	4	4	3.00							
HP1200C	3	3	4	3	4	4	2.50	4	4	4	4	4	4	
HP1600C	4	4	4	3	4	3	3.88	3	3	3	4	4	3	
BJ-200e	3	3				2	-							
BJC-600	3	3	3	3	4	4	3.25	4	4	4	4	4	4	
BJC 4200	3	3	4	3	4	4	3.50	3	3	4	4	4	4	
BJC 4200 photo	3	4	4	3	3	4	3.63	4	4	4	4	4	4	
BJC 4200 Neon	3	4	4	3	4	4	3.75	4	4	4	4	4	4	
Epson Stylus Color	4	3	4	3	3	4	3.63	4	4	4	4	4	4	
Epson 2	4	3	4	3	4	2	3.50	2	2	2	2	2	2	
Epson 500	4	4	4	3	2	4	3.75	4	4	4	4	4	4	
Epson 1500	4	4	4	3	4	3	3.88	3	3	2	4	3	3	

**Table 4**  
**Drying Time and Image Permanence -- Example 9**

PRINTER	BLACK				COLOR				
	Drying Time (min:sec)		Image Permanence		Drying Time (min:sec)		Image Permanence		
	A2 Text	B2 Area Fill	B3 Optical Density	E1 Drip Test	C2 Text	D4 Area Fill	Yellow	Cyan	Magenta
HP 500C	0	2:10	1.58	0.212	0	0	0.09	0.102	0.13
HP 560C	0	0	1.49	0.26	0	0			
HP 682C	0		1.39	0.044	0	0			
HP 693C	0		1.35	0.059	0		0.24	0.344	0.284
HP850C	0		1.33	0.042	0		0.198	0.21	0.224
HP1200C	0	0	1.19	0.03	0		0.242	0.39	0.3
HP-1600C	0	0	1.38	0.04	0	0	0.256	0.52	0.3
BJ-200e	0		1.48	0.37					
BJC-600	0		1.36	0.252	0				
BJC 4200	0	0	1.54	0.284	0	0			
BJC 4200 Photo	0	0	1.5	0.188	0	3:00	0.056	0.052	0.0925
BJC 4200 Neon	0	0	1.62	0.298	0	0	0.068	0.09	0.1
Epson Stylus Color	0	0	1.38	0.252	0	0			
Epson 2	0	0	1.19	0.16	0	0			
Epson 500	0	0	1.62	0.288	0	0			
Epson 1500	0		1.3	0.302	0	2:35			

**Table 5**  
**Print Quality (PQ) and Color Intensity -- Comparative Example 2**

PRINTER	BLACK		COLOR					Total Numerical	COLOR INTENSITY						
	TEXT	AREA FILL	TEXT	AREA FILL			AREA FILL D3								
				B1 Overall PQ	C1 Overall PQ	D1 Overall PQ	D2 C to C Bleed		D3 Color Intensity	Blue	Green	Yellow	Cyan	Magenta	Red
HP 500C	3	3	3	3	3	4	3	3.13	2	2	3	3	3	2	2
HP 560C	3	3	3	3	3	4	2	3.00	2	2	3	2	3	2	2
HP 682C	2	3	2	3	3	4	3	2.63	3	3	3	3	3	3	3
HP 693C	3	4	4	4	4	4	2	3.50	2	2	2	2	2	2	2
HP 850C	1	1	1	1	1	3	2	1.38							
HP1200C	3	3	4	3	4	4	3	3.38	3	3	2	3	3	3	3
HP1600C	3	4	4	3	4	4	3	3.63	3	3	3	3	3	3	3
BJ-200e	3	3					3	1.88							
BIC-600	4	3	4	3	3	2	2	3.25	2	2	2	2	2	2	2
BIC 4200	4	4	4	4	2	1	2	3.38	2	2	2	2	2	2	2
BIC 4200 photo	4	4	4	1	1	1	2	3.38	1	1	1	1	1	1	1
BIC 4200 Neon	4	4	4	4	4	2	3	3.63	4	4	4	4	4	4	4
Epson Stylus Color	4	3	4	3	3	2	2	3.25	2	2	2	2	2	2	2
Epson 2	4	3	3	3	2	3	1	3.00	1	1	1	1	1	1	1
Epson 500	4	3	3	3	3	1	3	3.00	2	2	2	2	2	2	2
Epson 1500	4	3	3	3	2	2	2	3.00	2	2	3	3	3	2	2

**Table 6**  
**Drying Time and Image Permanence -- Comparative Example 2**

	BLACK				COLOR				
	Drying Time (min:sec)		Image Permanence		Drying Time (min:sec)		Image Permanence		
	A2 Text	B2 Area Fill	B3 Optical Density	E1 Drip Test	C2 Text	D4 Area Fill	Yellow	Cyan	Magenta
PRINTER									
HP 500C	0	0	1.31	0.232	0	0	0.098	0.136	0.172
HP 560C	0	0	1.35	0.184	0	0			
HP 682C	1:45	1:50	1.35	0.042	1:45	2:10	0.27	0.32	0.31
HP 693C	:30	1:00	1.35	0.006	1:00	1:15	0.23	0.292	0.282
HP850C	:30	1:00	1.73	0.078	30	1:00	0.338	0.3	0.234
HP1200C	1:00	1:30	1.26	0.02	15:00	>30:00	0.038	0.1	0.104
HP-1600C	1:30	1:30	1.63	0.04	15:00	>30:00	0.102	0.075	0.1025
BJ-200e	0	0	1.19	0.22					
BJC-600	0	:20	1.03	0.22	0	:30			
BJC 4203	0	:15	1.25	0.326	10	:30			
BJC 4200 Photo	0	0	1.34	0.228	0	8:30	0.15	0.202	0.082
BJC 4200 Neon	0	0	1.14	0.392	0	0	0.072	0.28	0.21
Epson Stylus Color	2:00	2:50	1.05	0.175	3:45	4:00			
Epson 2	0	:50	1.06	0.348	40	1:10			
Epson 500	3:00	5:00	1.22	0.27	3:50	5:15			
Epson 1500	0	0	1.16	0.54	2:30	3:00			

**Table 7**  
**Print Quality (PQ) and Color Intensity -- Comparative Example 3**

PRINTER	BLACK		COLOR				Total Numerical	COLOR INTENSITY							
	TEXT	AREA FILL	TEXT	AREA FILL				AREA FILL D3							
				B1 Overall PQ	C1 Overall PQ	D1 Overall PQ		D2 C to C Bleed	D3 Color Intensity	Blue	Green	Yellow	Cyan	Magenta	Red
HP 500C	3	4	3	3	4	3	3.36	3	3	3	3	3	3	3	3
HP 560C	3	4	3	3	4	3	3.36	3	3	3	3	3	3	3	3
HP 682C	2	4	3	3	4	4	3.25	4	4	4	4	4	4	4	4
HP 693C	3	4	3	3	4	3	3.38	3	3	3	3	3	3	3	3
HP 850C	2	3	3	3	4	3	2.88								
HP1200C	3	3	4	4	4	2	3.25	2	2	2	2	2	2	2	2
HP1600C	4	4	4	4	4	3	3.88	3	3	3	3	3	3	3	3
BJ-200e	3	4				3	2.13								
BJC-600	3	3	3	3	4	3	3.13	3	3	3	3	3	3	3	3
BJC 4200	4	4	4	4	4	4	4.00	4	4	4	4	4	4	4	4
BJC 4200 photo	4	4	3	3	3	4	3.63	3	3	2	3	3	3	3	3
BJC 4200 Neon	4	4	4	4	4	3	3.88	3	3	1	3	3	3	3	3
Epson Stylus Color	4	3	3	3	4	4	3.50	4	4	4	4	4	4	4	4
Epson 2	4	3	4	4	4	2	3.50	2	2	1	2	2	2	1	1
Epson 500	3	4	3	3	3	3	3.25	3	3	2	3	3	3	2	2
Epson 1500	4	4	4	4	4	4	4.00	4	4	4	4	4	4	4	4



**Table 8**  
**Drying Time and Image Permanence -- Comparative Example 3**

PRINTER	BLACK				COLOR				
	Drying Time (min:sec)		Image Permanence		Drying Time (min:sec)		Image Permanence		
	A2 Text	B2 Area Fill	B3 Optical Density	E1 Drip Test	C2 Text	D4 Area Fill	Yellow	Cyan	Magenta
HP 500C	0	1:20	1.4	0.044	0	0	0.032	0.028	0.06
HP 560C	0	0	1.39	0.108	0	0			
HP 682C	0	1:00	1.29	0.018	0	0	0.352	0.294	0.292
HP 693C	:15	:30	1.38	0.02	:15	:30	0.348	0.234	0.202
HP850C	0	:30	1.15	0.02	0	0	0.468	0.206	0.242
HP1200C	0	0	1.06	0.018	0	0	0.35	0.364	0.238
HP-1600C	0	0	1.31	0.008	0	0	0.414	0.336	0.238
BJ-200e	0	0	1.35	0.238					
BJC-600	0	0	1.31	0.132	0	:20			
BJC 4200	0	:20	1.43	0.048	0	0			
BJC 4200 Photo	0	0	1.42	0.048	0	3:50	0.038	0.024	0.192
BJC 4200 Neon	0	0	1.41	0.054	0	0	0	0.035	0.048
Epson Stylus Color	0	0	1.35	0.306	1:25	3:25			
Epson 2	0	:20	1.1	0.064	0	0			
Epson 500	0	:30	1.42	0.302	0	1:30			
Epson 1500		1:00	1.35	0.142	0	1:20			

The ink-receptive coated label product of Example 9 generally performed better than the uncoated label product (C-2) and comparable to the matte finish polyester product (C-3), with some differences in color intensities and drying times. Overall color intensities and drying times for Example 9 were comparable to C-3 and much better than C-2. Color intensities for Example 9 were better than both C-2 and C-3, while overall print quality was comparable to that of C-3 and even slightly better than that of C-2. A significant improvement in waterfastness was seen for Example 9 over C-2, but not C-3.

#### **Water Resistance of Imprinted Vinyl Products**

To simulate exposure of an ink-jet imprinted coated construction to rainy or wet conditions expected to be encountered outdoors by many wide format products, an ink-receptive, polyvinyl chloride construction (Example 10) was prepared, imaged with an ink-jet printer, and evaluated for color quality, both before and after twenty-four hour immersion in water.

#### **Example 10**

In Example 10, several samples of 3.4 mil, calendered, white polyvinyl chloride film were coated with an ink-receptive composition (prepared as in Example 9), to a dry coat weight of about 50 to 55 g/m<sup>2</sup>, in a reverse roll coater. The samples were imprinted with a series of images by running the samples through a four-color ENCAD NOVAJET PRO Printer containing ENCAD GO (graphic outdoor) ink. Color images with 100%, 50% and 25% ink coverage were printed on different samples, for each of the following colors: cyan, yellow, magenta, black, red (magenta + yellow), blue (magenta + cyan), and green (cyan + yellow). The printed image on each sample was evaluated for lightness and chromaticity using the L\*a\*b\* color space (also referred to as the CIELAB color space), one of the uniform color spaces defined by the CIE in 1976. Lightness and chromaticity measurements were taken with a Colortron II color measurement device, made by Light Source Computer Images, Inc. (San Rafael, CA). The lightness measurement, L\*, typically ranges from +100 to 0, with a higher number being whiter or brighter; a\* (chromaticity (red to green)) and b\* (chromaticity (yellow to blue)) chromaticity coordinates each range from +100 to -100. A more complete description of the L\*a\*b\* color space is found in Appendix A ("Precise Color Communication," Minolta Camera Co., Ltd., pp 18, 46, 47). Three separate measurements of each of L\*, a\* and b\* were taken for each color image, and the average (mean) of the three values was recorded. After each sample was printed and evaluated for color space, it was placed in a vessel containing deionized water for 24 hours, allowed to dry, and new color space measurements were taken. The degree of color difference is denoted  $\Delta E^*$ , defined by the

equation:

where  $\Delta L^*$ ,  $\Delta a^*$  and  $\Delta b^*$  are, respectively, the differences between the post- and pre-immersion values of  $L^*$ ,  $a^*$  and  $b^*$ . A small  $\Delta E^*$  is preferred and indicates little change in color after immersion. The results are presented in Table 9.

**Table 9**  
**Water Resistance of Imprinted Samples**

Color	Before Immersion			After 24 Hour Water Soak			
	$L^*$	$a^*$	$b^*$	$L^*$	$a^*$	$b^*$	$\Delta E^*$
100% Cyan	67.62	-23.29	-39.52	65.17	-23.64	-40.40	2.63
100% Yellow	93.46	-15.05	72.88	92.64	-15.31	75.73	2.98
100% Magenta	59.95	55.19	-19.14	57.70	57.67	-18.87	3.36
100% Black	28.50	0.30	0.75	27.22	0.43	1.35	1.42
50% Cyan	79.59	-18.56	-27.02	78.65	-18.80	-27.19	0.98
50% Yellow	94.69	-15.16	55.77	94.46	-15.79	58.54	2.85
50% Magenta	72.05	40.01	-17.73	70.62	41.56	-18.09	2.14
50% Black	59.41	0.15	-2.04	57.82	0.17	-0.74	2.05
25% Cyan	89.53	-8.76	-14.41	88.35	-8.86	-13.92	1.28
25% Yellow	96.12	-9.79	26.88	95.41	-10.05	27.96	1.32
25% Magenta	84.22	21.33	-11.87	83.03	21.31	-11.30	1.32
25% Black	79.42	0.06	-2.70	78.12	0.06	-1.82	1.57
100% Red	59.88	40.03	30.21	57.86	42.08	31.16	3.03
100% Green	62.28	-56.10	29.17	60.58	-57.10	28.09	2.25
100% Blue	44.98	18.73	-39.26	43.10	18.82	-39.19	1.88
100% CMY	41.80	-7.62	8.28	39.58	-6.46	6.01	3.38
50% Red	71.26	27.30	21.93	70.16	27.60	24.82	3.11
50% Green	77.35	-41.29	24.62	76.09	-42.37	27.01	2.91
50% Blue	61.84	15.29	-34.35	59.78	17.85	-35.07	3.36
50% CMY	60.04	-3.27	2.06	58.33	-2.72	3.62	2.38
25% Red	83.46	12.26	13.21	82.75	12.13	14.21	1.23
25% Green	88.48	-20.37	13.89	87.64	-20.57	15.20	1.57

25% Blue	78.02	11.13	-21.11	76.54	11.73	-21.23	1.60
25% CMY	77.17	0.53	2.88	76.09	0.79	4.39	1.87

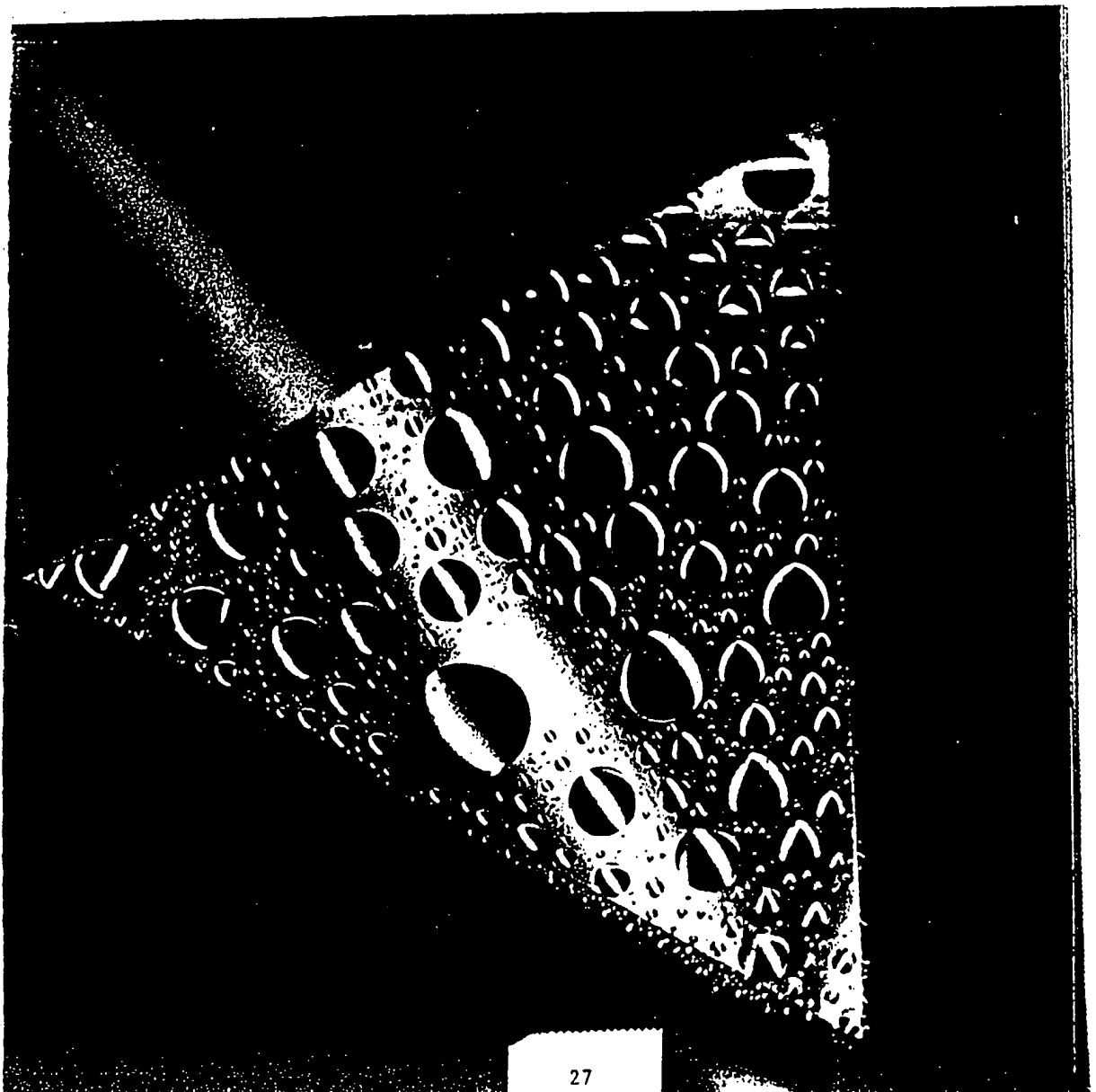
As indicated in Table 9, the ink-receptive coated product of Example 10 exhibited little difference in image quality after 24 hour immersion in water, evidencing significant water resistance.

Throughout the text and the claims, use of the word "about" in relation to a range of numbers is intended to modify both the low and the high values stated.



# PRECISE COLOR COMMUNICATION

COLOR CONTROL FROM FEELING TO INSTRUMENTATION





**Minolta Camera Co., Ltd.**

**Minolta Corporation  
Head Office**

**Minolta Canada Inc.  
Head Office**

**Minolta GmbH**

**Minolta France S.A.**

**Minolta (UK) Limited**

**Minolta Austria Gesellschaft m.b.H.**

**Minolta Camera Benelux B.V.**

**Minolta (Schweiz) AG**

**Minolta Hong Kong Limited**

**Minolta Singapore (Pte) Ltd.**

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**Riedhof V, Riedstrasse 6 8953 Dietikon-Zürich, Switzerland**

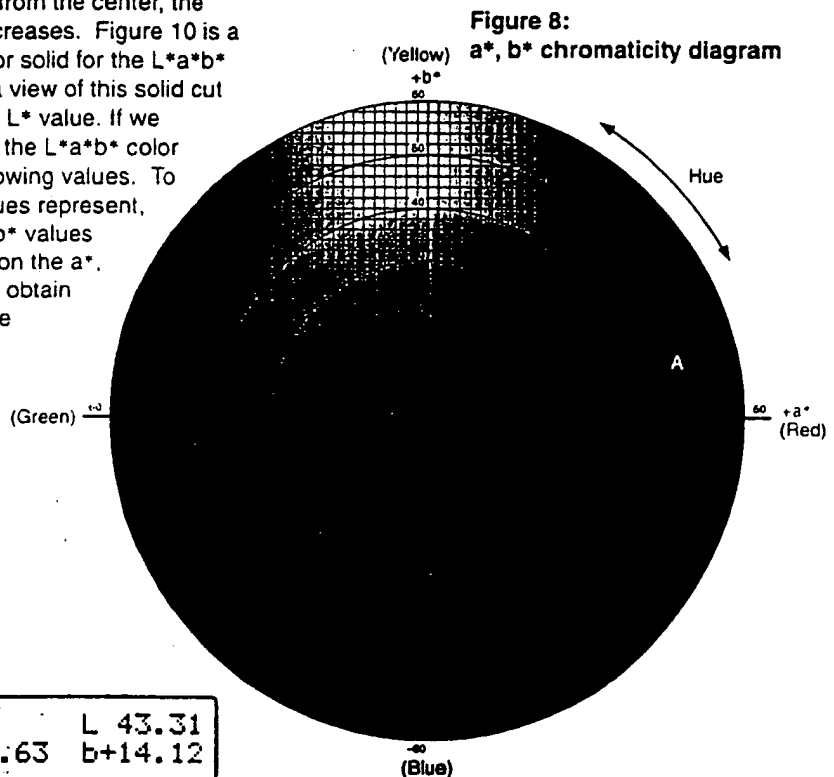
**Room 208, 2/F, Eastern Center, 1065 King's Road, Quarry Bay, Hong Kong**

**10, Teban Gardens Crescent, Singapore 2260**

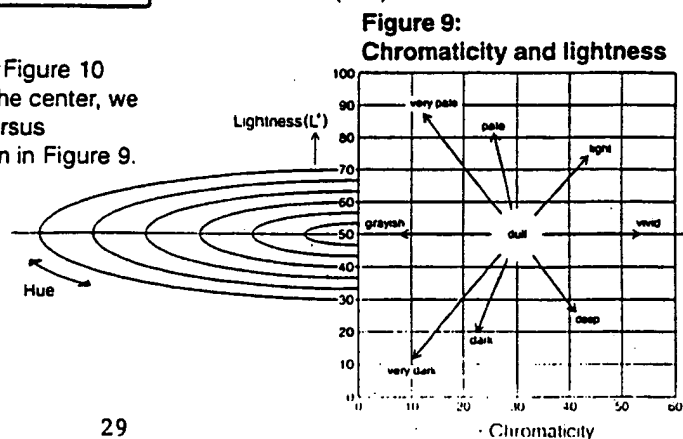
The  $L^*a^*b^*$  color space (also referred to as CIELAB) is presently one of the most popular color space for measuring object color and is widely used in virtually all fields. It is one of the uniform color spaces defined by CIE in 1976 in order to reduce one of the major problems of the original  $Yxy$  color space: that equal distances on the  $x, y$  chromaticity diagram did not correspond to equal perceived color differences. In this color space,  $L^*$  indicates lightness and  $a^*$  and  $b^*$  are the chromaticity coordinates. Figure 8 shows the  $a^*, b^*$  chromaticity diagram. In this diagram, the  $a^*$  and  $b^*$  indicate color directions:  $+a^*$  is the red direction,  $-a^*$  is the green direction,  $+b^*$  is the yellow direction, and  $-b^*$  is the blue direction. The center is achromatic; as the  $a^*$  and  $b^*$  values increase and the point moves out from the center, the saturation of the color increases. Figure 10 is a representation of the color solid for the  $L^*a^*b^*$  color space; Figure 8 is a view of this solid cut horizontally at a constant  $L^*$  value. If we measure the apple using the  $L^*a^*b^*$  color space, we obtain the following values. To see what color these values represent, let's first plot the  $a^*$  and  $b^*$  values ( $a^*=+47.63$ ,  $b^*=+14.12$ ) on the  $a^*, b^*$  diagram in Figure 8 to obtain point A, which shows the chromaticity of the apple.



001	L 43.31
a+47.63	b+14.12

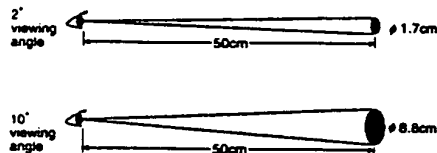


Now, if we cut the color solid of Figure 10 vertically through point A and the center, we obtain a view of chromaticity versus lightness, part of which is shown in Figure 9.



### 2° Standard Observer and 10° Supplementary Standard Observer

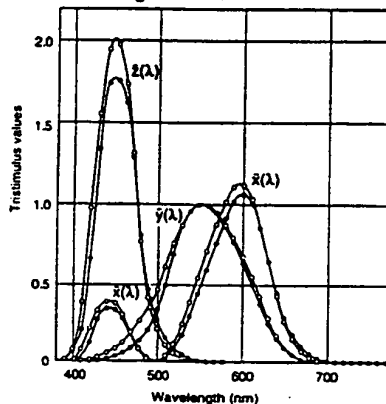
The color sensitivity of the eye changes according to the angle of view (object size). The CIE originally defined the standard observer in 1931 using a 2° field of view, hence the name 2° Standard Observer. In 1964, the CIE defined an additional standard observer, this time based upon a 10° field of view; this is referred to as the 10° Supplementary Standard Observer. To give an idea of what a 2° field of view is like compared to a 10° field of view, at a viewing distance of 50cm a 2° field of view would be a  $\phi 1.7\text{cm}$  circle while a 10° field of view at the same distance would be a  $\phi 8.8\text{cm}$  circle. Most of the information in this booklet is based on the 2° Standard Observer. The 2° Standard Observer should be used for viewing angles of 1° to 4°; the 10° Supplementary Standard Observer should be used for viewing angles of more than 4°.



### Color-Matching Functions

The color-matching functions are the tristimulus values of the equal-energy spectrum as a function of wavelength. These functions are intended to correspond to the sensitivity of the human eye. Separate sets of three color-matching functions are specified for the 2° Standard Observer and 10° Supplementary Standard Observer.

Color-matching functions



● 2° Standard Observer  
○ 10° Supplementary Standard Observer

### XYZ Tristimulus Values (CIE 1931)

Tristimulus values determined based on the color-matching functions  $\bar{x}(\lambda)$ ,  $\bar{y}(\lambda)$ , and  $\bar{z}(\lambda)$  defined in 1931 by CIE; also referred to as 2° XYZ tristimulus values. They are suitable for a viewing angle of 4° or less and are defined for reflecting objects by the following formulas:

$$X = K \int_{380}^{780} S(\lambda) \bar{x}(\lambda) R(\lambda) d\lambda$$

$$Y = K \int_{380}^{780} S(\lambda) \bar{y}(\lambda) R(\lambda) d\lambda$$

$$Z = K \int_{380}^{780} S(\lambda) \bar{z}(\lambda) R(\lambda) d\lambda$$

$$K = \frac{100}{\int_{380}^{780} S(\lambda) \bar{y}(\lambda) d\lambda}$$

where

$S(\lambda)$ : Relative spectral power distribution of the illuminant

$\bar{x}(\lambda)$ ,  $\bar{y}(\lambda)$ ,  $\bar{z}(\lambda)$ : Color-matching functions for CIE 2° Standard Observer (1931)

$R(\lambda)$ : Spectral reflectance of specimen

### X<sub>10</sub> Y<sub>10</sub> Z<sub>10</sub> Tristimulus Values (CIE 1964)

Tristimulus values determined based on the color-matching functions  $\bar{x}_{10}(\lambda)$ ,  $\bar{y}_{10}(\lambda)$ , and  $\bar{z}_{10}(\lambda)$  defined in 1964 by CIE; also referred to as 10° XYZ tristimulus values. They are suitable for a viewing angle of more than 4° and are defined for reflecting objects by the following formulas:

$$X_{10} = K \int_{380}^{780} S(\lambda) \bar{x}_{10}(\lambda) R(\lambda) d\lambda$$

$$Y_{10} = K \int_{380}^{780} S(\lambda) \bar{y}_{10}(\lambda) R(\lambda) d\lambda$$

$$Z_{10} = K \int_{380}^{780} S(\lambda) \bar{z}_{10}(\lambda) R(\lambda) d\lambda$$

$$K = \frac{100}{\int_{380}^{780} S(\lambda) \bar{y}_{10}(\lambda) d\lambda}$$

where

$S(\lambda)$ : Relative spectral power distribution of the illuminant

$\bar{x}_{10}(\lambda)$ ,  $\bar{y}_{10}(\lambda)$ ,  $\bar{z}_{10}(\lambda)$ : Color-matching functions for CIE 10° Supplementary Standard Observer (1964)

$R(\lambda)$ : Spectral reflectance of specimen



### xyz Chromaticity Coordinates

The xyz chromaticity coordinates are calculated from the XYZ tristimulus values according to the following formulas:

$$x = \frac{X}{X + Y + Z}$$

$$y = \frac{Y}{X + Y + Z}$$

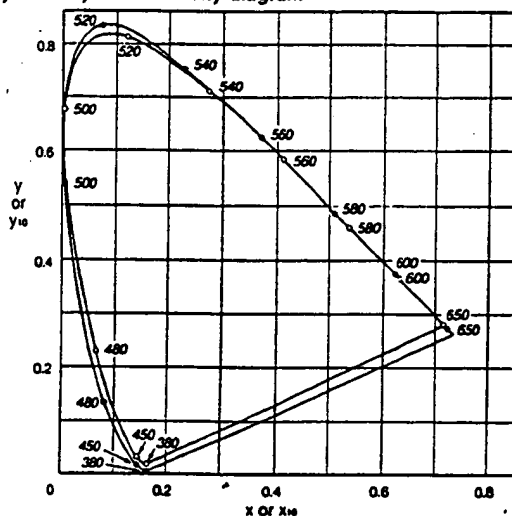
$$z = \frac{Z}{X + Y + Z} = 1 - x - y$$

If the above formulas are used with the  $X_{10}$   $Y_{10}$   $Z_{10}$  tristimulus values, the chromaticity coordinates would be  $x_{10}$   $y_{10}$   $z_{10}$ .

### xy and $x_{10}$ $y_{10}$ Chromaticity Diagram

Two-dimension diagram on which the xy or  $x_{10}$   $y_{10}$  chromaticity coordinates can be plotted.

xy and  $x_{10}$   $y_{10}$  chromaticity diagram



- For 2° Standard Observer (CIE 1931)
- For 10° Supplementary Standard Observer (CIE 1964)

### $L^*a^*b^*$ Color Space

The  $L^*a^*b^*$  color space (also referred to as the CIELAB space) is one of the uniform color spaces defined by the CIE in 1976. The values of  $L^*$ ,  $a^*$ , and  $b^*$  are calculated according to the formulas below:

Lightness variable  $L^*$ :

$$L^* = 116 \left( \frac{Y}{Y_n} \right)^{1/3} - 16$$

Chromaticity coordinates  $a^*$  and  $b^*$ :

$$a^* = 500 \left[ \left( \frac{X}{X_n} \right)^{1/3} - \left( \frac{Y}{Y_n} \right)^{1/3} \right]$$

$$b^* = 200 \left[ \left( \frac{Y}{Y_n} \right)^{1/3} - \left( \frac{Z}{Z_n} \right)^{1/3} \right]$$

where

$X, Y, Z$ : Tristimulus values XYZ (for 2° Standard Observer) or  $X_{10}Y_{10}Z_{10}$  (for 10° Supplementary Standard Observer) of the specimen

$X_n, Y_n, Z_n$ : Tristimulus values XYZ (for 2° Standard Observer) or  $X_{10}Y_{10}Z_{10}$  (for 10° Supplementary Standard Observer) of a perfect reflecting diffuser.

If  $X/X_n$ ,  $Y/Y_n$ , or  $Z/Z_n$  is less than 0.008856, the above equations are changed as described below:

$$\left( \frac{X}{X_n} \right)^{1/3} \text{ is replaced by } 7.787 \left( \frac{X}{X_n} \right) + \frac{16}{116}$$

$$\left( \frac{Y}{Y_n} \right)^{1/3} \text{ is replaced by } 7.787 \left( \frac{Y}{Y_n} \right) + \frac{16}{116}$$

$$\left( \frac{Z}{Z_n} \right)^{1/3} \text{ is replaced by } 7.787 \left( \frac{Z}{Z_n} \right) + \frac{16}{116}$$

Color difference  $\Delta E^*_{ab}$  in the  $L^*a^*b^*$  color space, which indicates the degree of color difference but not the direction, is defined by the following equation:

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

where

$\Delta L^*$ ,  $\Delta a^*$ ,  $\Delta b^*$ : Difference in  $L^*$ ,  $a^*$ , and  $b^*$  values between the specimen color and the target color.

## WHAT IS CLAIMED IS:

- 5           1.     A coatable, ink-receptive composition, comprising:  
            a pigment dispersed in or mixed with a binder comprising an ethylene-vinyl acetate  
emulsion polymer and at least one water soluble, cationic polymer.
2.     A composition as recited in claim 1, wherein the ethylene-vinyl acetate  
10    emulsion polymer has a solids content of from about 40 to 75%.
3.     A composition as recited in claim 1, wherein the ethylene-vinyl acetate  
emulsion polymer is present in an amount of from about 15 to 70% by weight (dry weight) of  
the composition.
- 15           4.     A composition as recited in claim 1, wherein the emulsion polymer is stabilized  
with polyvinyl alcohol and/or a nonionic surfactant.
5.     A composition as recited in claim 1, wherein the ethylene-vinyl acetate  
20    emulsion polymer is carboxylated.
6.     A composition as recited in claim 1, wherein at least one cationic polymer is a  
quaternary ammonium polymer.
- 25           7.     A composition as recited in claim 1, wherein at least one cationic polymer is  
selected from the group consisting of (i) a polymerized diallyldimethylammonium compound  
and (ii) a quaternary dimethylaminoethyl acrylate or methacrylate copolymerized with at  
least one hydroxy-lower organic acrylate or methacrylate.
- 30           8.     A composition as recited in claim 1, wherein the at least one cationic polymer is  
associated with counterions selected from the group consisting of halides, dimethyl sulfate,  
and mixtures thereof.
- 35           9.     A composition as recited in claim 1, wherein the water soluble, cationic  
polymer is present in an amount of from about 5 to 50% by weight (dry weight) of the  
composition.

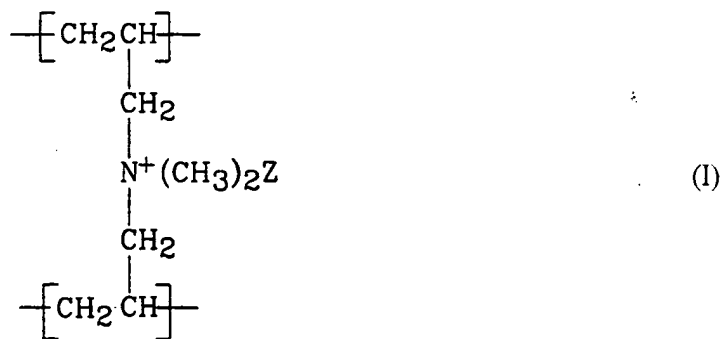
10. A composition as recited in claim 1, wherein the binder comprises an ethylene-  
vinyl acetate emulsion polymer, a first water soluble, quaternary ammonium polymer, and a  
5 second water soluble, quaternary ammonium polymer.

11. A composition as recited in claim 10, wherein the first water soluble quaternary  
polymer is a poly-(diallyldimethylammonium) compound.

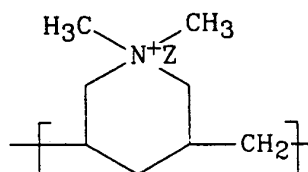
12. A composition as recited in claim 11, wherein the  
poly(diallyldimethylammonium) compound contains counterions selected from the group  
consisting of halides, dimethyl sulfate anion, and mixtures thereof.

13. A composition as recited in claim 12, wherein the halide is chloride.

14. A composition as recited in claim 10, wherein the first water soluble,  
quaternary ammonium compound comprises a polymer having repeat units of the formulas  
(I), (II) or (III)



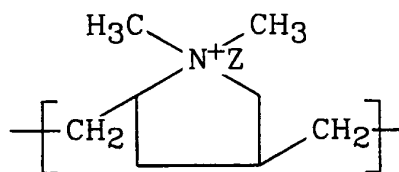
5



(II)

10

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(III)

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25

or mixtures thereof, where Z is a monovalent or divalent counterion.

15. A composition as recited in claim 10, wherein the second water soluble, quaternary polymer is a quaternary copolymer of dimethylaminoethyl acrylate or methacrylate and at least one hydroxy-lower organic acrylate or methacrylate.

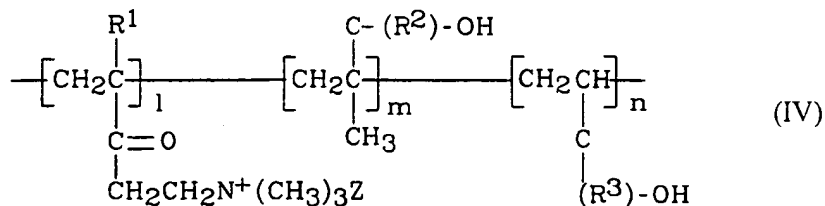
16. A composition as recited in claim 15, wherein the at least one hydroxy-organic alkyl acrylate or methacrylate is selected from the group consisting of hydroxyethyl acrylate, hydroxyethyl methacrylate, and mixtures thereof.

17. A composition as recited in claim 15, wherein the quaternary copolymer of dimethylaminoethyl acrylate or methacrylate and at least one hydroxy-lower organic acrylate

or methacrylate has the formula (IV)

5

10



15 wherein  $\text{R}_1$  is hydrogen or methyl;  $\text{C}-(\text{R}^2)-\text{OH}$  and  $\text{C}-(\text{R}^3)-\text{OH}$  are, independently, lower alkyl, alkenyl, alkynyl, or ether, substituted with a hydroxyl group at a primary or secondary carbon;  $l > 0$ ;  $m \geq 0$ ;  $n \geq 0$ , provided that  $m$  and  $n$  are not both zero; and  $\text{Z}$  is a monovalent or divalent counterion.

20 18. A composition as recited in claim 1, wherein the binder further comprises at least one nonionic and/or cationic surfactant.

19. A composition as recited in claim 1, wherein the binder further comprises an ethoxylated nonionic surfactant and a cationic surfactant comprising hexadecyl  
25 trimethylammonium chloride.

20. A composition as recited in claim 18, wherein the at least one nonionic or cationic surfactant is present in a total amount of up to about 10% by weight (dry weight) of the composition.

30

21. A composition as recited in claim 1, wherein the pigment comprises an inorganic pigment.

22. A composition as recited in claim 21, wherein the pigment comprises an  
35 amorphous silica gel.

23. A composition as recited in claim 1, wherein the pigment is present in an amount of from about 20 to 60% by weight (dry weight) of the composition.

24. A composition as recited in claim 1, further comprising a second pigment.
- 5 25. A composition as recited in claim 24, wherein the second pigment is a colloidal dispersion silica.
26. A composition as recited in claim 1, wherein the binder further comprises a crosslinker.
- 10 27. A composition as recited in claim 26, wherein the crosslinker is selected from the group consisting of polyisocyanates, melamine formaldehyde resins, and urea formaldehyde resins.
- 15 28. A coatable, ink-receptive composition, comprising, on a dry weight basis:  
about 15 to 70% of an ethylene vinyl acetate emulsion polymer;  
about 5 to 50% of at least one water soluble, cationic polymer;  
about 20 to 60% of one or more pigments; and  
up to about 10% of one or more surfactants.
- 20 29. An ink-receptive composition as recited in claim 28, further comprising a crosslinker.
- 25 30. An ink-receptive construction, comprising:  
a face stock or label stock, coated on at least one surface with an ink-receptive composition as recited in claim 28.
- 30 31. An ink-receptive construction, comprising:  
a substrate, coated on one or both surfaces with an ink-receptive composition comprising a pigment dispersed in or mixed with a binder, the binder comprising an ethylene-vinyl acetate emulsion polymer and at least one water soluble, cationic polymer.
- 35 32. An ink-receptive construction as recited in claim 31, wherein at least one cationic polymer is selected from the group consisting of (i) a polymerized diallyldimethylammonium compound and (ii) a dimethylaminoethyl acrylate or methacrylate copolymerized with at least one hydroxy-lower organic acrylate or methacrylate.

33. An ink-receptive construction as recited in claim 31, wherein the emulsion polymer contains polyvinyl alcohol and/or a nonionic surfactant.

5

34. An ink-receptive construction as recited in claim 31, wherein the binder further comprises a nonionic and/or cationic surfactant.

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35. An ink-receptive construction as recited in claim 31, wherein the ink-receptive composition is applied to the substrate at a coat weight of greater than about 5 g/m<sup>2</sup>, measured after drying.

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36. An ink-receptive construction as recited in claim 30, wherein the substrate comprises a paper, film, cardboard or corrugated board substrate.

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37. An ink-receptive construction as recited in claim 31, wherein the substrate comprises a cast, extruded, or coextruded film of plastic selected from the group consisting of polystyrene, polyvinyl chloride, polyester, nylon, polyolefin and blends thereof, or a coextruded polyolefin-polybutylene terephthalate sandwich.

38. An ink-receptive construction as recited in claim 31 wherein the substrate comprises a label assembly.

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39. An ink-receptive construction as recited in claim 38, wherein the label assembly comprises (i) a face stock having at least one inner surface and at least one outer surface, (ii) a pressure-sensitive adhesive adhered to at least one inner surface of the face stock, and (iii) a removable release liner abutting the pressure-sensitive adhesive, wherein the ink-receptive coating is coated on an outer surface of the face stock.

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40. An ink-receptive construction as recited in claim 39, wherein a plurality of die cuts extend through the face stock and adhesive.

35

41. An imprinted construction, comprising:  
a face stock or label stock, coated on at least one surface with an ink-receptive composition as recited in claim 1, imprinted with a black and/or color image.

42. An imprinted construction as recited in claim 41, wherein the imprinted image is water-resistant.

43. An imprinted construction as recited in claim 41, wherein the face stock or label stock comprises polyvinyl chloride or coextruded polyolefin-polybutylene terephthalate.

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44. A water resistant, wide format or narrow format graphic construction suitable for use indoors or outdoors, comprising:

a substrate having at least first and second surfaces;

10 an ink-receptive coating on a first surface of the substrate, the coating comprising a pigment dispersed in or mixed with a binder comprising an ethylene-vinyl acetate emulsion polymer and at least one water soluble, cationic polymer; and

an inked image, imprinted on the coated substrate.

15 45. A water-resistant graphic construction as recited in claim 44, wherein the inked imaged is an ink jet image.

46. A water-resistant graphic construction as recited in claim 44, further comprising an adhesive coated on or applied to a second surface of the substrate.

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47. A water-resistant graphic image, comprising:

a graphic image construction adhered to an object, the construction comprising (a) an imprintable substrate having first and second surfaces, (b) an ink-receptive composition coated on the first surface of the imprintable substrate, the composition comprising a pigment dispersed in or mixed with a binder comprising an ethylene-vinyl acetate emulsion polymer and at least one water soluble cationic polymer, and (c) an adhesive coated on or applied to the second surface of the imprinted substrate and adhered to the object.

25

48. A process for producing a water-resistant image for wide format or narrow format graphics, comprising:

30

coating a substrate with an ink-receptive composition comprising a pigment dispersed in or mixed with a binder comprising an ethylene vinyl acetate emulsion polymer and at least one water soluble, cationic polymer; and

printing an image on the coated substrate.

35



# INTERNATIONAL SEARCH REPORT

Int ional Application No  
PCT/US 98/15153

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 B41M5/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>WO 97 01448 A (KIMBERLY CLARK CO) 16 January 1997</p> <p>see page 3, line 26 - line 35 see page 4, line 21 - page 5, line 24 see page 6, line 16 - line 17 see example 1 see claim 1</p> <p style="text-align: center;">--- -/-</p>	<p>1, 3, 4, 6, 8, 9, 18, 20, 21, 23, 28, 30, 31, 33-38, 41, 42, 44-48</p>



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

14 October 1998

Date of mailing of the international search report

23/10/1998

Name and mailing address of the ISA

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Authorized officer

Martins Lopes, L

# INTERNATIONAL SEARCH REPORT

Int. l. Application No.  
PCT/US 98/15153

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 613 525 A (MIYAMOTO SHIGEHICO ET AL) 23 September 1986	1,6-8, 21,24, 31, 36-38, 41-45,48
A	see column 3, line 34 - line 35 see column 4, line 28 - line 66 see column 5, line 6 - line 23 see claims 1-7 ---	10-17
X	EP 0 705 704 A (CANON KK) 10 April 1996  see page 3, line 55 - page 4, line 40 see claims 1-5 ---	1,6-9, 18,20, 21,24, 26,27, 31,32, 34,35, 37,38, 41-45,48
X	EP 0 199 874 A (MEAD CORP) 5 November 1986  see page 5, line 28 - line 31 see page 6, line 10 see page 6, line 27 see page 7, line 8 - page 8, line 17 see page 9, line 19 - line 22 see page 10, line 18 - line 22 see claims 1-4 ---	1,6-9, 21,31, 32, 36-38, 41-45,48
X	EP 0 655 346 A (MITSUBISHI PAPER MILLS LTD) 31 May 1995  see page 3, line 45 - line 46 see page 6, line 56 see page 7, line 20 - line 31 see claim 3 ---	1,18,20, 21,23, 31,36, 38,41, 42,44, 45,48
A	US 5 501 902 A (KRONZER FRANCIS J) 26 March 1996 see column 4, line 39 - line 46 see column 8, line 59 - line 64 see column 5, line 65 - column 6, line 14 ---	1-48
	-/--	

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/15153

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PATENT ABSTRACTS OF JAPAN  vol. 009, no. 229 (M-413),  14 September 1985  &amp; JP 60 083882 A (MITSUBISHI SEISHI KK),  13 May 1985  see abstract</p> <p style="text-align: center;">-----</p>	10-17

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/15153

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9701448	A	16-01-1997	AU 6396796 A	30-01-1997
			CA 2222209 A	16-01-1997
			EP 0837778 A	29-04-1998
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